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STRUCTURE AND MAGNETIC PROPERTIES OF MECHANICALLY ALLOYED $Fe_{3-x}AlCr_x$ POWDERS

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Abstract

Mixtures of elemental powders of $Fe_{3-x}AlCr_x$ composition, where $x \in (0.8\text{ -}1.2)$ were mechanically alloyed in the AGO-2U planetary ball mill. Obtained powders consist of particles with median size of 0.5-1.6 μm; increase in the Cr content results in the decrease in the size of particles. According to the X-ray data, all of the as-milled alloys possess a single-phase disordered b.c.c. structure. Increase in Cr content results in the decrease in the grain size of alloys, whereas the dependence of the lattice parameter on the chemical composition is not conclusive. Mössbauer spectra for most of the alloys shows that iron atoms in this alloys, in spite of the fact that only one phase was detected using the X-ray diffraction, exist both in ferromagnetic and non-ferromagnetic conditions.

Introduction

The aim of our study was to investigate the structure of mechanically alloyed powders of Al-Fe-Cr system in the concentration ratios near Fe_3AlCr Heusler alloys composition. Alloys of this composition may be promising for application as magnetic materials, for instance, in the local magnetic hyperthermia. Structures of $L2_1$, $C1_b$, A2 and B2 types can be realized in this system, at that the $L2_1$ corresponds to Heusler alloys [1].

No study of mechanically alloyed powder of this system was found in literature, whereas the cast alloys of this system were studied in some papers, but the results of investigations are contradictory. So, for $Fe_{3-x}Cr_xAl$ composition a decrease in the lattice parameter with the increase in chromium content was observed [2], whereas for $Fe_{7-x}Cr_xAl_3$ alloys increase in the chromium content results in the increase of the lattice parameter [3].

There are some published papers devoted to the magnetic properties of the alloys of this system. According to [4], the Curie temperature in binary disordered FeAl alloys decreases with increase in the aluminum content; it was found that at Fe concentration of ~30 at.% the alloys behave as anti-ferromagnetic. In the study [5], a linear concentration dependence of Curie temperature was obtained for $Fe_{3-x}Cr_xAl$ alloys. Magnetic disorder increases with increase in Cr concentration due to the formation of clusters. Clusters screen Fe atom from the next influences, results in the increase in paramagnetic peak in Mössbauer spectra.

It is known that magnetic properties of iron containing transitions metals alloys are sensitive to the effects of a local atomic environment [5-8]. $Fe_{3-x}Cr_xAl$ alloys with $D0_3$ structure are suitable for investigations of the effect of the iron atom environment on the magnetic properties. As it was shown in [9], for this type of alloys the geometrically equal positions of iron atoms can possess different magnetic moments. Data on the Mössbauer study of these alloys are also collected in the paper [9]. Four sextets which correspond to various environments of iron atoms were found in this paper. In study reference [10] where $Fe_{3x}Cr_xAl$ alloys was studied, it was observed that hyperfine fields does not depend on chromium concentration; for $x < 0,2$, and for $x > 0,3$ the hyperfine fields increases noticeably. This fact confirms the assumption that chromium atoms first of all take positions of iron and reduce nuclear streamlining in alloys. As it was found from neutron diffraction data, chromium atoms are distributed between positions A, B and C in these alloys.

Magnetic properties of the rapidly quenched $Fe_{66}Cr_{12}Al_{22}$ alloy were studied in the paper [11] and it was found that hyperfine fields increases by 14 % after 72 hours of annealing, and then remains invariable. In [12], disordered Heusler $Fe_{3-x}AlCr_x$ ($0 \le x \le 1$) alloys were studied. Samples were annealed for 72 hours at 800 ^oC, and then kept at 200 ^oC for the same time with cooling in the furnace. X-ray analysis has shown the B2 type of ordering. Coexistence of a paramagnetic and ferromagnetic part was observed in the temperature range from 40 to 296 K. Such phenomenon also was observed for alloy Fe_2MnAl, for which the coexisting of antiferromagnetic and ferromagnetic parts was observed [13].

Experimental

Elemental powders of aluminum (99.5 %), iron (99.5 %) and chromium (99.85 %) were used as the starting materials. Mechanical alloying was carried out using an AGO-2M high-energy ball mill with the water cooling. The total time of milling of each sample was 4 h. The structure of specimens was examined using the X-ray diffraction analysis. The tracing of diffraction spectra was carried out using a DRON-4-07 X-ray diffractometer with monochromatized CoK_α emission. To calculate the obtained spectra, a special package of programs

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was used. The lattice parameters were calculated to the accuracy of $\Delta a/a = 0.0015$. Scanning electron microscope HITACHI TM-1000 was used to investigate powders macrostructure and size distribution. Chemical composition of samples was determined using scanning electron microscope HITACHI S-800. Room temperature Mössbauer measurements were carried out by means of a constant acceleration spectrometer with a ^{57}Co:Cr source. The isomer shifts were calculated with respect to the centroid of the α-Fe spectrum. Current minimization routines were used to obtain the best fit of the spectra. Temperatures of Curie point were measured by thermo-magnetic method using differential measuring transformer. Samples were placed in the hermetic quartz ampoules, then absorption of oxygen and nitrogen was realized by preliminary heating of magnesium getter inside. Temperature was measured by thermocouple buried into the sample powder.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the as-milled alloys. Similar patterns were observed for all investigated compositions, i.e. all investigated powders possess single-phase disordered b.c.c. structure of A2 type. Concentration dependence of the lattice parameter, calculated from the diffraction data, is shown in Fig. 2. It is seen that for x value in the range of 0.8 to 0.95, a lattice parameter decrease, which is in disagreement with the results of paper [2]. The presented dependence has nonmonotonic character, which can be explained by a deviation of real stoichiometric composition from the initial. The lattice parameter for Fe_2AlCr sample nearly coincides with the results in [12].

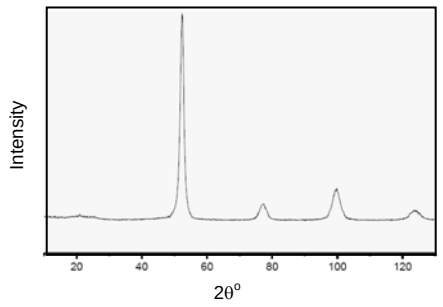

Figure 1. X-ray diffraction patterns of $Fe_{2.05}AlCr_{0.95}$ alloy

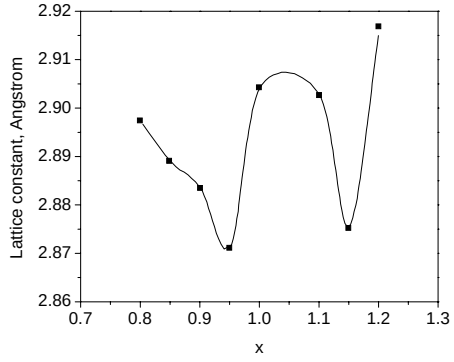

Figure 2. Concentration dependence of lattice parameter

Figure 3 shows a typical micrograph for investigated samples. It is seen that the shape of powder particles are nearly spherical and possess wide size distribution. Average particle size was calculated using the ImageExpert 2.35 program for every samples. Figure 4 show the concentration dependence of the particles size. Average size of particles for all investigated samples was found to be near 1.4 μm and particles with size less than 0,5 μm are also presents in the samples in significant amount. This allows proposing that mechanically alloyed magnetic materials are suitable for using in magnetic fluid hyperthermia.

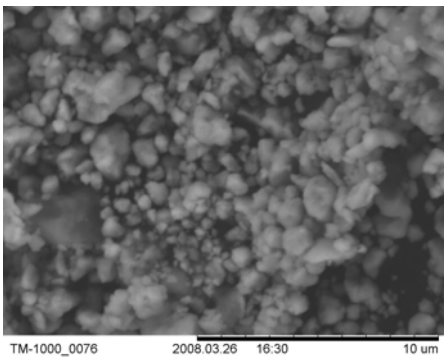

Figure 3. SEM micrograph for sample with x=1.15 (Magnification 10000x)

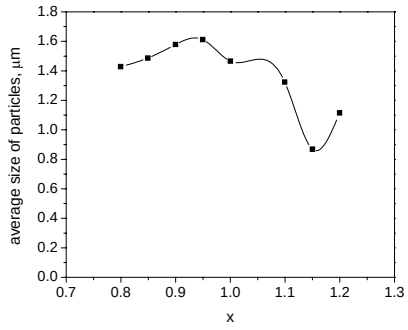

Figure 4. Concentration dependence of average size of particles

The element analysis was performed for all produced alloys. Both large-scale area and local analysis were performed. It was observed that samples are chemically non-uniform, and their composition differs from the intended composition. It means that used conditions of mechanical alloying does mot results in the formation of homogeneous solid solutions. Results of the analysis allow explaining the asymmetry of peaks of X-ray diffraction patterns.

Mössbauer investigations of obtained powders were performed to study the local environment of iron atoms. Figure 5 shows Mössbauer spectra of the obtained samples. For all compositions, excluding $Fe_{2.05}AlCr_{0.95}$ and $Fe_{1.8}AlCr_{1.2}$, a coexistence of the ferromagnetic and paramagnetic component was observed. Completely ferromagnetic condition of $Fe_{2.05}AlCr_{0.95}$ sample can be explained by sufficiently high concentration of iron in this alloy. Paramagnetic condition of the

$Fe_{1.8}AlCr_{1.2}$ sample (here sextet is present only as traces) also can be explained by chemical composition. It is possible to propose that the Curie temperature for this sample is below the room temperature. For other samples correlation between intensity of sextet lines and iron concentration in alloy was observed. Obtained spectra were fitted with eight sextets and one doublet. Hyperfine fields are in good agreement with the values reported in [9] for disordered alloys. However, the results shown here differ from [12], which may be a result of the deviation in concentration.

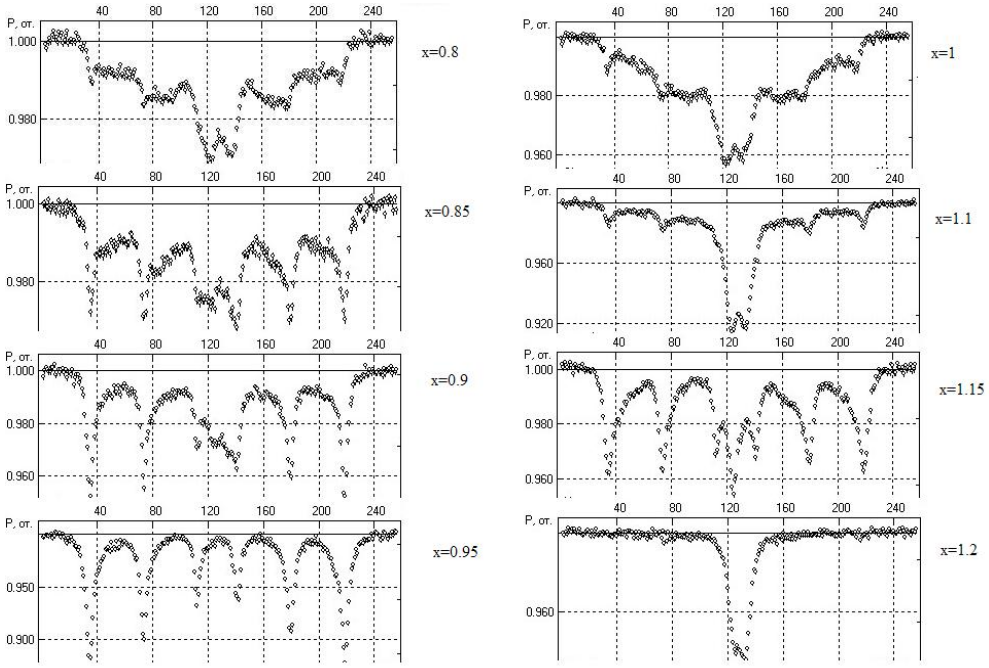

Figure 5. Mössbauer spectra of the as-milled alloys

Such large amount of sextets is a result of various kinds of environment of iron atoms. Besides, at the sample there are atoms of iron which are surrounded by iron atoms only. These results are in the good agreement with the chemical analysis and the X-ray data. Absence of a short-distance ordering, which was observed using the Mössbauer spectroscopy shows that obtained alloys are really completely disordered. In paper [12], where thermally ordered alloys were studied, only two sextets which correspond to chromium atoms taking positions with two-three next atoms of iron (owing to the ordered structure of alloys) were observed. For samples with x= 0.85, 0.9, 0.95, and 1.15, it was observed a sextet with hyperfine field of 33 T, which corresponds to iron atoms gland, surrounded by only iron atoms. Existence of this component is a result on the inhomogeneity of obtained solid solution for these compositions. Comparing this data with the results of the local chemical analysis, it is possible to conclude that the sizes of pure iron inclusions are not great (less than 5 μm), and the chemical analysis can not sense them. Based on the obtained size of these iron areas we propose that they are not connected with contamination of processed powder by the material of balls and vials, and represent the residual unreacted initial iron.

Thermomagnetic measurements have been carried out for investigated samples. Magnetization curve typical for these alloys is presented in Fig. 6. The measured Curie temperatures were found to be enough close to the temperature of magnetic transition of iron. In addition, a hysteresis in the magnetization of samples was observed: at heating the magnetization are lower, and Curie temperatures are higher than at and cooling. Such difference was observed for all the investigated alloys (Fig. 7). It means that the local ordering is reversible and varies depending on temperature. The similar phenomenon was observed in amorphous alloys by [14].

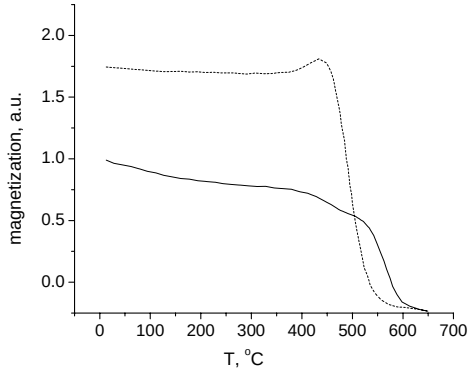

Figure 6. Typical thermomagnetic curve for the studied samples

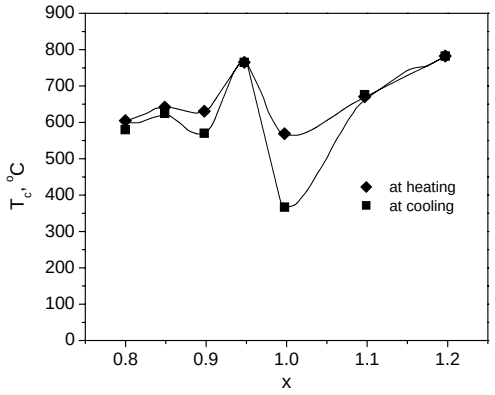

Figure 7. Concentration dependence of Curie temperatures, measured during heating and cooling

Conclusions

Mechanically alloyed samples of $Fe_{3-x}AlCr_x$ composition were investigated. The focus was on composition and phase structure of mechanically alloyed $Fe_{3-x}AlCr_x$ powders investigated. It was found that all samples are single-phase with b.c.c. structure. Granulometric analysis of the received powders shows that the average size of powders varies from 0,8 to 1,6 μm. Mössbauer spectroscopy and local chemical analysis shows that used mode of mechanical alloying does not allow to obtain chemically homogeneous material. Alloy which is probably not ferromagnetic at a room temperature was obtained. To use the mechanically alloyed powder of the investigated system in the magnetic hyperthermia, a number of problem, such as uniformity of the particle size, homogeneity of chemical compositions and controlled decrease of the Curie temperature have to be solved.

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